



Applicant's Docket No. U 013852-8

**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of: Julian Graham PRICE, et al.  
Serial No.: 10/056,232 Group No.: 1764  
Filed: January 25, 2002 Examiner:  
For: NATURAL GAS CONVERSION TO HYDROCARBONS AND AMMONIA

Commissioner for Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

**TRANSMITTAL OF CERTIFIED COPY**

Attached please find the certified copy of the foreign application from which priority is claimed for this case:

Country: South Africa

Application  
Number: 99/4879

Filing Date: 29 July 1999

**WARNING:** "When a document that is required by statute to be certified must be filed, a copy, including a photocopy or facsimile transmission of the certification is not acceptable." 37 C.F.R. 1.4(f) (emphasis added).

**CERTIFICATE OF MAILING (37 C.F.R. 1.8a)**

I hereby certify that this correspondence is, on the date shown below, being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to the Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450.

Date: May 5, 2004

Signature

Clifford J. Mass

(type or print name of person certifying)

(Transmittal of Certified Copy—page 1 of 2) 5-4

Reg. No.

Tel. No.: (    )

Customer No.:



---

**SIGNATURE OF PRACTITIONER**

Clifford J. Mass, 30086, (212) 708-1890  
(type or print name of practitioner)

---

P.O. Address

---

c/o Ladas & Parry LLP  
26 West 61<sup>st</sup> Street  
New York, N.Y. 10023

*NOTE: "The claim to priority need be in no special form and may be made by the attorney or agent, if the foreign application is referred to in the oath or declaration, as required by § 1.63." 37 C.F.R. 1.55(a).*

*Sertifikaat*

PATENTKANTOOR REPUBLIC OF SOUTH AFRICA

DEPARTEMENT VAN  
HANDEL EN NYWERHEID



*Certificate*  
REPUBLIEK VAN SUID-AFRIKA PATENT OFFICE

DEPARTMENT OF TRADE  
AND INDUSTRY

Hiermee word gesertifiseer dat  
This is to certify that

the documents annexed hereto are true copies of:

Application form P.1 and provisional specification of South  
African Patent Application No. 99/4879 as originally filed in  
the Republic of South Africa on 29 July 1999 in the name  
of SASOL TECHNOLOGY (PROPRIETARY) LIMITED for an  
invention entitled: "NATURAL GAS CONVERSION TO  
HYDROCARBONS AND AMMONIA".

Geteken te  
Signed at

PRETORIA

in die Republiek van Suid-Afrika, hierdie  
in the Republic of South Africa, this

14th

dag van  
day of

June 2002

*12/06/02*  
Registrateur van Patente  
Registrar of Patents

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978

APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT

[Section 30 (1) - Regulation 22]

Revenue stamps or revenue franking machine impression

Official date stamp

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

OFFICIAL APPLICATION NO.		
21	01	994879

(i)	APPLICANT'S OR AGENT'S REFERENCE
	F223

FULL NAME(S) OF APPLICANT(S)	
(ii)	71 SASOL TECHNOLOGY (PTY) LTD

ADDRESS(ES) OF APPLICANT(S)		REGISTRAR OF PATENTS, DESIGNS, TRADE MARKS AND COPYRIGHT
(iii)	1 STURDEE AVENUE, ROSEBANK JOHANNESBURG	1999 -07- 29

TITLE OF INVENTION		REGISTRATEUR VAN PATENTE, MODELLE, HANDELSMERKE EN OUTEURSREG
(iv)	54 NATURAL GAS CONVERSION TO HYDROCARBONS AND AMMONIA	

(v)	The applicant claims priority as set out on the accompanying form P2. The earliest priority claimed is	
-----	---	--

(vi)	This application is for a patent of addition to Patent Application No.	21	01
------	--	----	----

(vii)	This application is a fresh application in terms of section 37 and is based on Patent Application No.	21	01
-------	---	----	----

This application is accompanied by:																																								
(viii)	<table border="1"> <tr> <td>X</td> <td>1.</td> <td>A single copy of a provisional <del>XXXXXXX</del> specification of 8 pages.</td> </tr> <tr> <td></td> <td>2.</td> <td>Drawings of sheets.</td> </tr> <tr> <td></td> <td>3.</td> <td>Publication particulars and abstract (form P8 in duplicate).</td> </tr> <tr> <td></td> <td>4.</td> <td>A copy of Figure of the drawings for the abstract.</td> </tr> <tr> <td></td> <td>5.</td> <td>An assignment of invention.</td> </tr> <tr> <td></td> <td>6.</td> <td>Certified priority document(s) (state number):</td> </tr> <tr> <td></td> <td>7.</td> <td>Translation of the priority document(s).</td> </tr> <tr> <td></td> <td>8.</td> <td>An assignment of priority rights.</td> </tr> <tr> <td></td> <td>9.</td> <td>A copy of the form P2 and the specification of SA Patent Application No.</td> </tr> <tr> <td></td> <td>10.</td> <td>A declaration and power of attorney form P3.</td> </tr> <tr> <td></td> <td>11.</td> <td>Request for ante-dating on form P4.</td> </tr> <tr> <td></td> <td>12.</td> <td>Request for classification on form P9.</td> </tr> <tr> <td>X</td> <td>13.</td> <td>Form P2 + copy</td> </tr> </table>	X	1.	A single copy of a provisional <del>XXXXXXX</del> specification of 8 pages.		2.	Drawings of sheets.		3.	Publication particulars and abstract (form P8 in duplicate).		4.	A copy of Figure of the drawings for the abstract.		5.	An assignment of invention.		6.	Certified priority document(s) (state number):		7.	Translation of the priority document(s).		8.	An assignment of priority rights.		9.	A copy of the form P2 and the specification of SA Patent Application No.		10.	A declaration and power of attorney form P3.		11.	Request for ante-dating on form P4.		12.	Request for classification on form P9.	X	13.	Form P2 + copy
X	1.	A single copy of a provisional <del>XXXXXXX</del> specification of 8 pages.																																						
	2.	Drawings of sheets.																																						
	3.	Publication particulars and abstract (form P8 in duplicate).																																						
	4.	A copy of Figure of the drawings for the abstract.																																						
	5.	An assignment of invention.																																						
	6.	Certified priority document(s) (state number):																																						
	7.	Translation of the priority document(s).																																						
	8.	An assignment of priority rights.																																						
	9.	A copy of the form P2 and the specification of SA Patent Application No.																																						
	10.	A declaration and power of attorney form P3.																																						
	11.	Request for ante-dating on form P4.																																						
	12.	Request for classification on form P9.																																						
X	13.	Form P2 + copy																																						

(ix)	74 Address for service:	HAHN & HAHN INC, 222 Richard Street, HATFIELD
------	-------------------------	---

Dated this 29 day of July 19 99

Signature of applicant(s) or agent

This duplicate will be returned to the applicant's address for service as proof of lodging but is not valid unless endorsed with an official stamp

REGISTRAR OF PATENTS, DESIGNS, TRADE MARKS AND COPYRIGHT
Received 1999-07-29
REGISTRATEUR VAN PATENTE, MODELLE, HANDELSMERKE EN OUTEURSREG

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
**PROVISIONAL SPECIFICATION**  
[Section 30 (1) - Regulation 27]

OFFICIAL APPLICATION NO.		
21	01	994879

LODGING DATE	
22	29/07/99

FULL NAME(S) OF APPLICANT(S)

71

**SASOL TECHNOLOGY (PTY) LTD**

FULL NAME(S) OF INVENTOR(S)

72

**JULIAN GRAHAM PRICE  
BARRY ANTHONY TINDALL**

TITLE OF INVENTION

54

**NATURAL GAS CONVERSION TO HYDROCARBONS AND AMMONIA**

## NATURAL GAS CONVERSION TO HYDROCARBONS AND AMMONIA

- 5 The present invention relates to an optimisation process for the production of hydrocarbons and ammonia.

### BACKGROUND OF THE INVENTION

- 10 Hydrocarbons are typically produced by contacting synthesis gas, comprising CO and H<sub>2</sub> as major components, with a preferred selective catalyst. Similarly, synthesis gas comprising N<sub>2</sub> and H<sub>2</sub> may be passed over a catalyst for the production of NH<sub>3</sub>. Both types of synthesis gas are produced from natural gas by reforming the gas at high temperature. The method of  
15 manufacture involves the use of steam reforming and autothermal reforming in various combinations. The process in which the synthesis gas is used for hydrocarbon production utilises a high purity O<sub>2</sub> stream in the reforming process, because the addition of inert gases (particularly N<sub>2</sub>) is generally considered detrimental to the process economics. The process in which the  
20 synthesis gas is used for NH<sub>3</sub> production utilises air in the reforming process. Care must be taken to remove all traces of CO from the synthesis gas as this specie causes ammonia catalyst poisoning.

- The ammonia synthesis process may be used in combination with a Fischer-Tropsch (FT) process. In the said process, hydrogen is removed from the  
25 Fischer-Tropsch tailgas stream for use in the ammonia synthesis process. However, it is only feasible if the conversion in the Fischer-Tropsch section is reasonably low and a catalyst active for the water gas shift is utilised in the Fischer-Tropsch reactor.

30

It is known in the art that under most conditions, the Fischer-Tropsch process requires a synthesis gas that contains H<sub>2</sub> and CO in a ratio at, or below, about 2. Conventional steam reforming and autothermal reforming

technologies produce synthesis gas at a ratio greater than this ideal. Various alternatives have been proposed to obtain the correct ratio. These involve recycling of CO<sub>2</sub> which can be extracted from various points in the synthesis loop or recycling the Fischer-Tropsch tailgas back to the reforming section.

- 5 Such methods are useful not only because they reduce the H<sub>2</sub>/CO ratio, but also because they increase the overall carbon utilisation in the process.

Conversely, ammonia synthesis requires a very high H<sub>2</sub>/CO ratio. This is adjusted even further after the reforming section by using shift converters, which convert CO and water into CO<sub>2</sub> and H<sub>2</sub>. A conventional ammonia process then extracts the CO<sub>2</sub> which is then vented to the atmosphere.

There is thus a need for optimising the conversion of natural gas to synthesis gas so that desired H<sub>2</sub>/CO ratios are obtained for use in both the production of hydrocarbons and the production of ammonia.

## SUMMARY OF THE INVENTION

- 20 The present invention provides a novel way for overcoming problems in the operation of existing ammonia – Fischer-Tropsch integrated plants.

In particular, the present invention relates to an optimisation process for the production of hydrocarbons and ammonia that significantly reduces the capital and operating costs for the said process.

More particularly, the present invention provides a method of combined hydrocarbon and ammonia production which reduces emission of CO<sub>2</sub> into the atmosphere. In the method, hydrogen is extracted from a reforming section of the Fischer-Tropsch process rather than being extracted from the tail gas stream, and is then fed into the ammonia synthesis reactor. Previously, hydrogen necessary for ammonia synthesis was produced using

shift reactions which also produced large amounts of  $\text{CO}_2$ , which were subsequently vented to the atmosphere. The hydrogen may be extracted from the reforming section by using known methods in the art.

5 According to the invention there is provided a method of converting natural gas to synthesis gas for the production of both hydrocarbons and ammonia, the method including the following steps:

extracting hydrogen from a reforming section of a Fischer-Tropsch process; and

10 feeding at least a portion of the extracted hydrogen to an ammonia synthesis reactor.

The hydrogen may be extracted from the reforming process until a  $\text{H}_2/\text{CO}$  ratio of the synthesis gas is lower than or equal to a preselected value, the  
15 value, for example, being 2.

High purity  $\text{H}_2$  is fed to the ammonia synthesis process and thus the danger of CO poisoning is eliminated. In a further embodiment, CO and/or  $\text{CO}_2$  are removed from the  $\text{H}_2$  rich stream and returned to the reforming section to  
20 produce synthesis gas suitable for the hydrocarbon synthesis.

According to a further embodiment of the invention there is provided an hydrocarbon produced according to the process described above.

25 According to yet a further embodiment of the invention there is provided ammonia produced according to the process described above.

According to yet a further embodiment of the invention there is provided a Fischer-Tropsch plant including an hydrogen extraction means for extracting  
30 hydrogen from a reforming section's product stream.

A connecting means may be provided to feed at least a portion of the

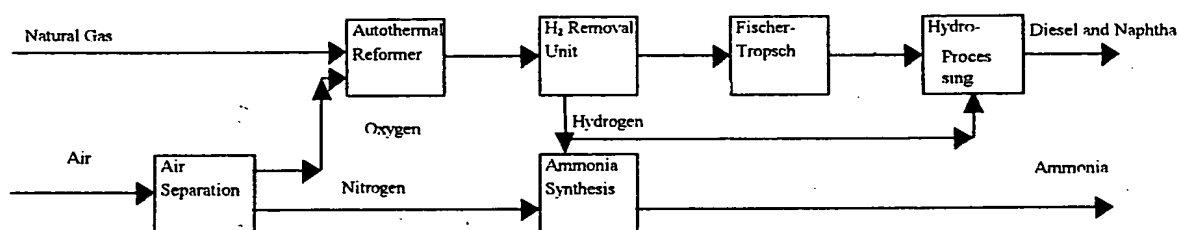


extracted hydrogen to an ammonia synthesis reactor.

The invention will now be illustrated further by way of the following non-limiting examples:

5

### Example 1



10

Natural gas is passed through an oxygen burning autothermal reformer. The oxygen is supplied from a cryogenic air separation facility. The reformer unit produces a synthesis gas with an H<sub>2</sub>/CO ratio of greater than 2.0. A hydrogen extraction unit is placed on the exit stream from the reformer or a portion thereof so as to adjust the H<sub>2</sub>/CO ratio to a value below 2. The synthesis gas is then sent to a Fischer-Tropsch reactor which operates at a total conversion level above 85%.

20

The excess hydrogen that has been removed above is further purified, compressed and sent to an ammonia synthesis reactor. Nitrogen, which is available at high purity from the cryogenic air separation unit is combined with the hydrogen and also sent to the ammonia plant.

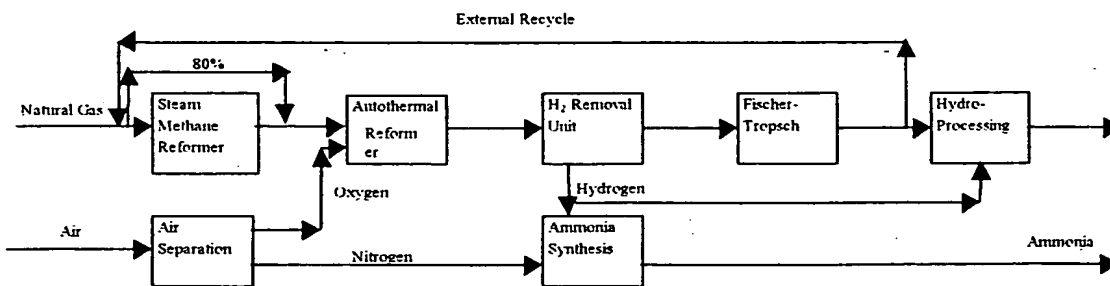
25

### Example 2

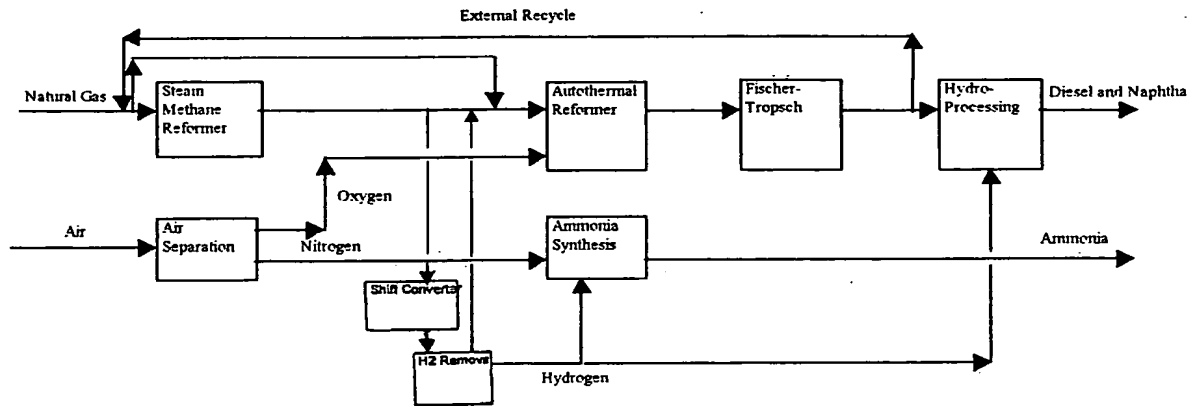
Natural gas mixed with a recycle stream from a Fischer-Tropsch reactor is sent to the reforming section of a Fischer-Tropsch plant. The reforming section consists of a steam reformer followed by an autothermal reformer. The natural gas stream is split, with a portion entering the steam reformer, while the majority enters the autothermal reformer. Hot synthesis gas from the steam reformer mixes with the bypass natural gas before entering the autothermal reformer.

A hydrogen extraction unit is placed on the exit stream from the autothermal reformer or a portion thereof so as to adjust the  $H_2/CO$  ratio to a value below 2. The synthesis gas is then sent to a Fischer-Tropsch reactor that operates at a total conversion level above 85%. Some of the Fischer-Tropsch tailgas is returned to the front of the reforming section. This can be utilised to further adjust the  $H_2/CO$  ratio as well as increasing the carbon utilisation of the process.

The excess hydrogen that has been removed is further purified, compressed and sent to an ammonia synthesis reactor. Nitrogen, which is available at high purity from the cryogenic air separation unit is combined with the hydrogen and also sent to the ammonia plant.



### Example 3



5

Natural gas mixed with a recycle stream from a Fischer-Tropsch reactor is sent to the reforming section of a Fischer-Tropsch plant. The reforming section consists of a steam reformer followed by an autothermal reformer.

- 10 The natural gas stream is split, with a portion entering the steam reformer, while the majority enters the autothermal reformer. The synthesis gas from the steam reformer is cooled and sent to a shift reactor which converts most of the CO and H<sub>2</sub>O into CO<sub>2</sub> and H<sub>2</sub>. The H<sub>2</sub> is then separated from the other gases. The hydrogen poor offgas is compressed and returned to the front end of the autothermal reformer. The split ratio between the steam reformer and autothermal reformer is adjusted so that the H<sub>2</sub>/CO ratio of the synthesis gas leaving the autothermal reformer is below 2. The synthesis gas is then sent to a Fischer-Tropsch reactor that operates at a total conversion level above 85%. Some of the Fischer-Tropsch tailgas is returned to the front
- 15 of the reforming section. This can be utilised to further adjust the H<sub>2</sub>/CO ratio as well as increasing the carbon utilisation of the process.
- 20

The excess hydrogen that has been removed is further purified, compressed and sent to an ammonia synthesis reactor. Nitrogen, which is available at high purity from the cryogenic air separation unit is combined with the

25

hydrogen and also sent to the ammonia plant.

The applicant believes that the invention is advantageous in that apart from the high total conversion obtained, substantial economic benefits also result, for example:

- 1) a reforming section for an ammonia plant is not required;
- 2) a desired  $H_2/CO$  ratio in the synthesis gas sent to the Fischer-Tropsch section may be achieved;
- 3) an  $H_2$  stream is extracted from the synthesis gas stream and thus  $CO_2$  which would be vented to atmosphere in a conventional ammonia facility remains in the Fischer-Tropsch loop, and is further used to adjust the synthesis gas ratio to the desired value;
- 4) conventional Fischer-Tropsch processes that aim to produce motor fuels additionally require a hydroprocessing section to upgrade the primary Fischer-Tropsch products into diesel. This requires a hydrogen source which incurs additional capital expenditure. However, the present invention does not require this additional hydrogen source, thus resulting in a substantial monetary saving.

The invention is not limited to the precise constructional details as herein described.

DATED THIS 29TH DAY OF JULY 1999

S.L. Chell - d  
HAHN & HAHN INC.  
Agent for Applicant